



## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

VERIFICATION OF TRANSLATION

In the Matter of Application for  
Letters Patent by Matsubayashi et al.  
U.S. Serial No. 10/507,013  
Filed: September 8, 2004

I, Keiji Tokieda, of 2-20-204, Kaitori 2-chome, Tama-shi,  
Tokyo, Japan, a translator, being duly sworn, depose and say:

1. That I am well acquainted with the Japanese and English languages; and
2. That the attached translation is a true translation into English of the Certified copy of the Japanese Patent Application No. 2002-64127 filed on March 8, 2002.
3. That all statements made of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 USC 1001, and that such false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated: November 2, 2005

  
Keiji Tokieda

Application No. 2002-064127

Document Name: Patent Application

Reference Number: P14010CA-H

Date of Submittance: March 8, 2002

To: Mr. Commissioner, Patent Office

Inventor:

Name: Hiroshi Matsubayashi

Address: c/o Technical Headquarters of Toyo Seikan Kaisha, Ltd.,  
1-1-70, Yako, Tsurumi-ku, Yokohama-shi, Kanagawa-ken

Inventor:

Name: Shozo Ichinose

Address: c/o Technical Headquarters of Toyo Seikan Kaisha, Ltd.,  
1-1-70, Yako, Tsurumi-ku, Yokohama-shi, Kanagawa-ken

Inventor:

Name: Takashi Iwai

Address: c/o Technical Headquarters of Toyo Seikan Kaisha, Ltd.,  
1-1-70, Yako, Tsurumi-ku, Yokohama-shi, Kanagawa-ken

Inventor:

Name: Takehito Ifuku

Address: c/o Tsurumi Branch of Technical Headquarters, Toyo  
Seikan Kaisha, Ltd., 1-8, Shitanoya-cho, Tsurumi-ku,  
Yokohama-shi, Kanagawa-ken

Patent Applicant:

Identification Number: 000003768

Name: Toyo Seikan Kaisha, Ltd.

Representative: Hirofumi Miki

Attorney:

Identification Number: 100067183

Patent Attorney

Name: Ikuo Suzuki

Indication of fee:

Account Number: 011729

Amount paid: ¥21,000

List of Submitted Documents:

Material Name: Specification

one copy

Material Name: Drawings

one copy

Material Name: Abstract

one copy

Number of General Authorization: 9002029

Request for proof: requested

[Designation of Document] SPECIFICATION

[Title of the Invention] PRESS-FORMED CAN MADE OF A PRE-COATED  
STEEL PLATE

[Claims]

[Claim 1] A can having excellent corrosion resistance formed by press-forming a pre-coated steel plate which is obtained by providing, on the surface of the steel plate on at least the side that becomes the inner surface of the can, a tin-plated layer containing tin in an amount of 0.5 to 12.0 g/m<sup>2</sup>, a silane coupling agent-treated layer containing Si in an amount of 0.8 to 18 mg/m<sup>2</sup>, and a thermoplastic polyester resin layer having a thickness of 8 to 42  $\mu$ m in this order from the side of the steel plate.

[Claim 2] A can according to claim 1, wherein part of said tin-plated layer on the side of the steel plate is a tin-iron alloy layer.

[Claim 3] A can according to claim 1 or 2, wherein said silane coupling agent-treated layer is a layer formed by the treatment by using an amino group-containing silane solution and/or an epoxy group-containing silane coupling agent solution.

[Claim 4] A can according to claim 1 or 2, wherein said silane coupling agent-treated layer is a layer formed by the treatment by using a mixed solution of a silane coupling agent containing an amino group and/or an epoxy group and a silane containing an organic substituent and a hydrolyzing alkoxyl group.

[Claim 5] A can according to claim 1 or 2, wherein said silane coupling agent-treated layer is a layer treated with a silane containing an organic substituent and a hydrolyzing alkoxyl group and is, then, treated with a silane coupling agent solution comprising an amino group-containing silane solution and/or an epoxy group-containing silane solution.

[Claim 6] A can having a reduced thickness according to any one of claims 1 to 5, wherein said thermoplastic polyester resin layer is a copolymerized resin film of a non-oriented polyethylene terephthalate.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to a can obtained by press-forming a steel plate coated with an organic resin. More specifically, the invention relates a can having a reduced thickness formed by using a surface-treated steel plate without using hexavalent chromium in the step of production and exhibiting excellent work adhesion property and corrosion resistance and is adapted to containing even highly corrosive contents.

[0002]

[Prior Art]

There has heretofore been used a two-piece can having a can wall and a can bottom formed integrally together without a junction portion in the can wall as a metal container for containing foods, beverages and aerosols. The two-piece can is formed through severe workings such as draw-ironing, draw working followed by stretch working, or draw working followed by stretch working and, further, ironing working (stretch-ironing).

The two-piece can has been produced by using a organic resin-coated steel plate obtained by coating a steel plate with an organic resin. From the standpoint of adhesion between the steel blank and the organic resin coating, work adhesion property and corrosion resistance after the working, in particular, an electrolytic chromium/chromium oxide-coated steel plate (tin-free steel, hereinafter referred to as TFS) has been extensively used for producing cans having a reduced thickness through a severe working in which a ratio represented by the following formula (1) and an average plate thickness reduction ratio represented by the following formula (2) are,

$$\text{Height (H) of can/can diameter (D)} \geq 1 \quad \text{--- (1)}$$

$$\{(\text{Initial plate thickness (t}_0\text{)} - \text{can wall thickness (t)})/\text{initial plate thickness (t}_0\text{)}\}$$

$$\times 100 \geq 20\% \quad \text{--- (2)}$$

[0003]

Japanese Unexamined Patent Publication (Kokai) No. 11-140691 teaches that a thermoplastic resin-coated steel plate obtained by forming a silane-treated film and a thermoplastic resin film on the TFS is suited for the use that is to be subjected to a severe working.

[0004]

[Problems to be Solved by the Invention]

The resin-coated steel plate using the above TFS features excellent adhesion of the coated layer even when subjected to the above severe working and exhibits excellent corrosion resistance after the working. However, the TFS is the one obtained through a cathodic electrolytic treatment in a treating solution containing hexavalent chromium followed by the washing with water. Though hexavalent chromium is not contained in the TFS surface-treating film which is the finally formed product, the treating solution contains harmful hexavalent chromium arousing many problems from the environmental point of view.

[0005]

That is, the drain water and exhaust gases of the treating solution containing hexavalent chromium must be completely treated so will not to be drained to the external side. Therefore, a tremendous amount of cost is required for the construction of the drain water treatment facility, exhaust gas treatment facility, and disposal of the waste. Besides, transporting the sludge of waste water and disposal thereof encounter stringent regulations. It has therefore been desired to produce thin cans through the above-mentioned severe working but by using a resin-coated steel plate obtained by using a metal blank other than the TFS.

[0006]

A tin plate (tin-plated steel plate) has long been used. Usually, however, the tin plate is obtained by plating tin followed by the chemical treatment such as being immersed in a solution of dichromic acid or the electrolysis in this solution. It is further widely effected to coat the tin plate

with a resin film in advance without, however, capable of withstanding the severe working for accomplishing a ratio of Height (H) of can/can diameter (D)  $\geq 1$  and a plate thickness reduction ratio of not smaller than 20%.

In the press-formed can using the tin plate, therefore, a protection film must be formed by applying a coating material after the press-forming, arousing the problems of disposal and treatment of the organic solvent, and coping with the worsening working environment. It has further been desired to shorten the step of coating.

It is, therefore, an object of the present invention to provide a can formed by press-forming a chrome-free steel plate coated with an organic resin featuring excellent film adhesion property, workability and corrosion resistance even when the thickness is reduced through severe working.

[0007]

[Means for Solving the Problem]

According to the present invention, there is provided a can having excellent corrosion resistance formed by press-forming a pre-coated steel plate which is obtained by providing, on the surface of the steel plate on at least the side that becomes the inner surface of the can, a tin-plated layer containing tin in an amount of 0.5 to 12.0 g/m<sup>2</sup>, a silane coupling agent-treated layer containing Si in an amount of 0.8 to 18 mg/m<sup>2</sup>, and a thermoplastic polyester resin layer having a thickness of 8 to 42  $\mu$ m in this order from the side of the steel plate.

[0008]

In the press-formed can of the present invention, it is desired that:

- (1) Part of said tin-plated layer on the side of the steel plate is a tin-iron alloy layer;
- (2) The silane coupling agent-treated layer is a layer formed by the treatment by using an amino group-containing silane solution and/or an epoxy group-containing silane coupling agent solution;

(3) The silane coupling agent-treated layer is a layer formed by the treatment by using a mixed solution of a silane coupling agent containing an amino group and/or an epoxy group and a silane containing an organic substituent and a hydrolyzing alkoxyl group;

(4) The silane coupling agent-treated layer is a layer treated with a silane containing an organic substituent and a hydrolyzing alkoxyl group and is, then, treated with a silane coupling agent solution comprising an amino group-containing silane solution and/or an epoxy group-containing silane solution; and

(5) The thermoplastic polyester resin layer is a copolymerized resin film of a non-oriented polyethylene terephthalate.

[0009]

[Embodiments of the Invention]

According to the press-formed can of the present invention, an important feature resides in the use of a pre-coated steel plate obtained by providing, on the surface of the steel plate on at least the side that becomes the inner surface of the can, a tin-plated layer containing tin in an amount of 0.5 to 12.0 g/m<sup>2</sup>, a silane coupling agent-treated layer, and a thermoplastic polyester resin layer in this order from the side of the steel plate.

[0010]

As shown in Fig. 1, the pre-coated steel plate of the present invention used for forming a press-formed can is a steel plate coated with an organic resin, comprising a tin-plated layer 2, a silane coupling agent-treated layer 3 and a thermoplastic polyester resin layer 4. The pre-coated steel plate is capable of providing a press-formed can that exhibits excellent workability, film adhesion property and excellent corrosion resistance after the working even when the thickness thereof is reduced through a severe working in which a ratio of the height of the can and the can diameter (above formula (1)) and the plate thickness reduction ratio of the can wall



(above formula (2)) are,

$$\text{Height of can (H)/can diameter (D)} \geq 1 \quad \text{--- (1)}$$

$$\{(\text{Initial plate thickness (t}_0) - \text{can wall thickness (t)})/\text{initial plate thickness (t}_0)\}$$

$$\times 100 \geq 20 \quad \text{--- (2)}$$

or even when it is subjected to a severe working such as flanging or necking.

[0011]

The TFS used as a metal blank of the organic resin-coated steel plate has a metal chromium layer and a chromium oxide hydrate layer formed on the steel plate exhibiting excellent adhesion to the resin coating and imparting corrosion resistance, resistance against rust and resistance against sulfur staining. According to the present invention, there are formed a tin-plated layer and a silane coupling agent-treated layer on the surface of the steel plate, to withstand severe working, to exhibit excellent adhesiveness to the organic resin coating and to exhibit corrosion resistance and rust resistance.

Namely, upon combining the tin-plated layer having excellent corrosion resistance and durability with the silane coupling agent-treated layer, it is allowed to improve adhesion of the thermoplastic polyester layer to the tin-plated layer to impart workability that withstands severe working.

Further, the layer treated with the silane coupling agent itself contributes to improving the durability and resistance against water while suppressing gases from permeating toward the tin-plated layer and, hence, suppressing the formation of an oxide film of the tin-plated layer. This prevents the deterioration of adhesion of the thermoplastic polyester resin layer caused by the formation and growth of the oxide film.

[0012]

[Pre-coated steel plate]

The press-formed can of the present invention has an important feature in that it is made of a pre-coated steel plate obtained by providing, on the surface of the steel plate on at

least the side that becomes the inner surface of the can, a tin-plated layer, a silane coupling agent-treated layer, and a thermoplastic polyester resin layer in this order as described above.

[0013]

[Tin-plated layer]

The tin-plated layer formed on at least one surface of the steel plate is the one which contains tin in an amount of 0.5 to 12.0 g/m<sup>2</sup>. By plating the steel plate with tin, the steel plate itself exhibits improved corrosion resistance. Upon being combined with the layer treated with the silane coupling agent, further, improved work adhesion property is obtained and, besides, improved corrosion resistance is obtained after the working.

[0014]

In the present invention as shown in Fig. 2, part of the tin-plated layer 2 on the steel plate 1 on the side of the steel plate may be a tin-iron alloy layer 2b; i.e., a two-layer constitution may be formed comprising the tin-plated layer 2a and the tin-iron alloy layer 2b.

To form the tin-plated layer as the two-layer constitution of tin-plated layer/tin-iron alloy layer, the steel plate is plated with a predetermined amount of tin followed by a reflow processing of conducting the heating at higher than the melting point of tin and cooling, so that part of the tin-plated layer on the side of the steel plate is transformed into the iron-tin alloy layer. It is desired that the alloy contains 5 to 50% of tin that is contained in the tin-plated layer.

By forming the tin-iron alloy layer as described above, improved work adhesion property is obtained and the steel plate itself exhibits improved corrosion resistance.

The tin-iron alloy layer in the tin-plated layer formed on the side of the steel plate may contain alloy components such as iron-tin-nickel or iron-tin-zinc in addition to tin-iron.

[0015]

The thickness of the tin-plated layer is, as described above; i.e, the content of tin is 0.5 to 12 g/m<sup>2</sup> and, particularly, 0.7 to 12 g/m<sup>2</sup>. That is, as will become obvious from the results of Examples appearing later, the pre-coated steel plate having a tin-plated layer containing tin in an amount within the above range exhibits excellent work adhesion property and excellent corrosion resistance. On the other hand, the pre-coated steel plate plated with tin in an amount of smaller than the above range (Comparative Example 1) exhibits poor work adhesion property at the flanging portion and develops corrosion in part of the double seamed portion, without offering satisfactory corrosion resistance. When the amount of tin exceeds the above range, the material of the can loses competitive power in economy though properties are not deteriorated.

Even when the tin-iron alloy layer is formed in a portion on the side of the steel plate through the reflow treatment, it is desired that the content of tin in the tin-plated layer formed on the steel plate prior to the reflow treatment lies within the above-mentioned range.

[0016]

[Silane coupling agent-treated layer]

The silane coupling agent-treated layer formed on the tin-plated layer works to improve the adhesion between the tin-plated layer and the thermoplastic polyester resin layer owing to the reaction group possessed by the silane coupling agent. Further, the silane coupling agent-treated layer helps improve the durability and resistance against water while suppressing the permeation of gases toward the tin-plated layer and, hence, suppressing the formation of an oxide film of the tin-plated layer. This prevents a deterioration in the adhesion to the organic resin coating layer caused by the formation and growth of the oxide film.

It is desired that the silane coupling agent-treated layer is so formed that the amount of Si is 0.8 to 18 mg/m<sup>2</sup> and, particularly, 1 to 15 mg/m<sup>2</sup>. When the amount of Si is smaller than the above range, the work adhesion property is poor and

satisfactory corrosion resistance is not obtained (Comparative Example 2). When the amount of Si is greater than the above range, the unreacted silane coupling agent undergoes the self-condensation making it difficult to obtain satisfactory work adhesion property or satisfactory corrosion resistance (Comparative Example 3).

[0017]

The silane coupling agent for forming the silane coupling agent-treated layer possesses a reaction group that chemically bonds to the thermoplastic polyester resin and a reaction group that chemically bonds to the tin-plated steel plate, and may comprise an organosilane having a reaction group such as amino group, epoxy group, methacryloxy group or mercapto group and a hydrolyzing alkoxyl group such as methoxy group or ethoxy group, or may comprise a silane having an organic substituent such as methyl group, phenyl group, epoxy group or mercapto group and a hydrolyzing alkoxyl group.

Concrete examples of the silane coupling agent that can be preferably used in the present invention include  $\gamma$ -APS ( $\gamma$ -aminopropyltrimethoxysilane),  $\gamma$ -GPS ( $\gamma$ -glycidoxypentyltrimethoxysilane), BTSPA (bistrimethoxysilylpropylaminosilane), and N- $\beta$  (aminoethyl)  $\gamma$ -aminopropyltrimethoxysilane.

[0018]

To form the silane coupling agent-treated layer on the tin-plated steel plate, the solution of the above-mentioned silane coupling agent is applied onto the tin-plated layer, or the tin-plated steel plate is immersed in the solution of the silane coupling agent and, then, an excess of solution is removed by using squeeze rolls. A preferred combination of the silane coupling agent solutions and the order of treatment are as described below.

(1) A layer is formed by the treatment by using an amino group-containing silane solution and/or an epoxy group-containing silane coupling agent solution.

(2) A layer is formed by the treatment by using a mixed

solution of a silane coupling agent containing an amino group and/or an epoxy group and a silane containing an organic substituent and a hydrolyzing alkoxyl group.

(3) A layer is formed by the treatment with a silane containing an organic substituent and a hydrolyzing alkoxyl group and, then, with a silane coupling agent solution comprising an amino group-containing silane solution and/or an epoxy group-containing silane solution.

[0019]

[Thermoplastic polyester resin layer]

In the present invention, the thermoplastic polyester resin layer formed on the silane coupling agent-treated layer to work as a protection film on the surface layer, little adsorbs fragrant components in the content and exhibits excellent barrier property against the corrosive components and excellent shock resistance.

Upon forming the thermoplastic polyester resin layer prior to forming a can, it is allowed to omit a step of coating for forming the protection film after the forming without accompanied by such problems as worsened working environment due to the organic solvent used for the coating and the disposal of the waste solution

[0020]

The polyester resin forming the thermoplastic polyester resin layer can be a widely known polyester resin derived from a carboxylic acid component and an alcohol component, and may be a homopolyester, a copolymerized polyester, or a blend of two or more kinds thereof.

As the carboxylic acid component, there can be used terephthalic acid, isophthalic acid, naphthalenedicarboxylic acid, P- $\beta$ -oxyethoxybenzoic acid, biphenyl-4,4'-dicarboxylic acid, diphenoxyethane-4,4'-dicarboxylic acid, 5-sodiumsulfoisophthalic acid, hexahydroterephthalic acid, adipic acid, sebacic acid, trimellitic acid, and pyromellitic acid.

As the alcohol component, further, there can be

exemplified ethylene glycol, 1,4-butanediol, propylene glycol, neopentyl glycol, 1,6-hexylene glycol, diethylene glycol, triethylene glycol, cyclohexane dimethanol, glycerol, trimethylolpropane, pentaerythritol, dipentaerythritol and sorbitan.

[0021]

Among the known thermoplastic polyester resins according to the present invention, it is particularly desired to use a polyethylene terephthalate type copolymer resin, i.e., an ethylene terephthalate type copolymerized polyester resin in which not less than 50 mol% of the carboxylic acid component is a terephthalic acid, and not less than 50 mol% of the alcohol component is an ethylene glycol component. Desirably, there can be used a polyethylene terephthalate/isophthalate containing 3 to 18 mol% of isophthalic acid as a carboxylic acid component.

It is desired that the polyester resin that is used has a molecular weight large enough for forming a film and has an inherent viscosity  $[\eta]$  as measured in the ortho-chlorophenol at 25°C of 0.6 to 1.2.

[0022]

In the pre-coated steel plate used in the invention, it is desired that the thermoplastic polyester resin layer has a thickness in a range of 8 to 42  $\mu\text{m}$  and, particularly, 10 to 40  $\mu\text{m}$  from the standpoint of balance between protecting the tin-plated steel plate and the workability. When the thickness of the thermoplastic polyester resin layer is smaller than the above range, the resin layer loses barrier property due to the reduced thickness, corrosion occurs due to the permeation of the content, cracks occur in the resin layer during the working for reducing the thickness, and the corrosion tends to occur at an increased probability. Further, when the thickness becomes greater than the above range, the resin layer itself exhibits increased rigidity, and the work adhesion property becomes poor in the portions subjected to the severe working such as necking portion or double-seamed portion (Comparative

Examples 8 and 9).

Any known means can be employed, such as extrusion coating method, cast film heat-adhesion method or film heat-adhesion method for forming the thermoplastic polyester resin layer on the steel plate on which there have been formed the tin-plated layer and the silane coupling agent-treated layer.

When the polyester film is used, the film is obtained by a T-die method or an inflation film-forming method. The film may be an undrawn film formed by the cast-forming method by quickly cooling the extruded film, or may be a biaxially stretched film produced by biaxially drawing the film at a drawing temperature successively or simultaneously and heat-setting the film after it has been drawn.

[0023]

In the present invention as described above, it is allowable to use either the non-oriented film or the biaxially oriented polyester film. It is, however, particularly desired to use the non-oriented polyester film.

Namely, use of the non-oriented (amorphous) polyester film makes it possible to obtain a laminate having a sufficiently large adhering force at a temperature lower than the melting point of the tin-plated layer, suppressing the damage in the silane coupling agent-treated layer caused by heating, and making it possible to accomplish excellent work adhesion property and corrosion resistance without impairing the effect of the treatment with the silane coupling agent.

[0024]

[Steel plate]

The steel plate used in the present invention may be a widely known cold rolled steel plate that has heretofore been used for producing cans, and has a plate thickness of about 0.1 to about 0.4 mm.

[0025]

[Layer constitution of the pre-coated steel plate]

As described above, the pre-coated steel plate used in the present invention has the alloy layer, the silane coupling

agent-treated layer and the thermoplastic polyester resin layer that are formed in this order on at least the surface of the steel plate that becomes the inner surface of the can. As required, further, there can be formed other layers. Namely, there can be formed the tin-plated layer and the thermoplastic polyester resin layer on the surface of the steel plate that becomes the outer surface of the can and like on the side of the inner surface and, besides, a white coated layer and a printed layer may be formed on the thermoplastic polyester resin layer.

[0026]

(Press-formed can)

To press-form a can according to the invention, the above pre-coated steel plate is subjected to the known press forming such as drawing, draw and redrawing, draw and wall ironing, draw and stretching, or draw and stretching and ironing (stretch-ironing) and, further, to the doming, trimming, flanging and necking, to obtain a two-piece can or a one-piece can without seam on the side surface.

The press-formed can of the present invention exhibits particularly excellent effects when its thickness is reduced being subjected to such a severe working that the ratio of height (H) of can/can diameter (D) is in a range of not smaller than 1 and, particularly, 1.1 to 3.0 and that the average plate thickness reduction ratio of the can wall  $\{( \text{initial plate thickness } (t_0) - \text{can wall plate thickness } (t) ) / \text{initial plate thickness } (t_0) \} \times 100$  is not smaller than 20% and, particularly, 25 to 70%.

[0027]

In producing the press can of the present invention, the thermoplastic polyester resin layer on the surface imparts a sufficient degree of lubricating property. To further enhance the lubricating property, however, a lubricant such as various oils and fats or waxes may be applied in small amounts to carry out the working on the lubricating solid surface.

[0028]



## [EXAMPLES]

The evaluation and the testing were as described below throughout Examples and Comparative Examples.

## 1. Work adhesion property.

A wax-type lubricant was applied onto both surfaces of the pre-coated steel plate, and a disk of a diameter of 155 mm was punched by press to obtain a shallow drawn cup. The shallow drawn cup was then subjected to the stretch ironing working to obtain a cup having a cup diameter of 66 mm, a cup height of 128 mm and an average plate thickness reduction ratio of the can wall portion of 55%. The cup was subjected to the doming according to an ordinary method, heat-treated at 215°C, and was, then, left to cool, followed by the trimming of the open edge portion, printing on the curved surface, baking and drying, necking and flanging to obtain a can of a reduced thickness having a capacity of 350 g. The can was observed by eyes for its state of adhesion of the metal blank and the resin-coated steel plate on the inner and outer surfaces of the can at the can wall portion, necking portion, and flanging portion, and was evaluated as follows:

○: No delamination.

△: Delamination area is smaller than 1 mm<sup>2</sup>.

X: Delamination area is not smaller than 1 mm<sup>2</sup>.

[0029]

## 2. Exposure of metal after the can has been formed.

The can after having been formed was filled with an aqueous solution containing 1% of sodium chloride, and an electric current flowing across the electrode and the can was measured by using an enamel rater and was regarded to be the exposure of a metal.

[0030]

## 3. Evaluation of testing of the can.

The can that has been formed was filled with 350 g of coke and was double seamed with an aluminum end. The can was stored at 37°C for 6 months.

\*Amount of iron dissolved.

The amount of iron in the content after stored and the amount of iron in the content before filled were measured by the atomic absorption method, and a difference therebetween was regarded to be the amount of dissolution of iron. The number of  $n$  was 24 cans, and an arithmetic average value of 24 cans was used.

\*Inner surface state of the can.

After stored, the content was removed, and the inner surface of the can was washed with water to observe the corroding state on the inner surface of the can and the discolored state by eyes and by using a microscope.

[0031]

(Example 1)

A tin-plated layer was formed on both surfaces of a cold rolled steel plate having a thickness of 0.18 mm and a tempering degree of DR7 by depositing tin in an amount of  $0.5 \text{ g/m}^2$  on each surface. The steel plate was then immersed in an aqueous solution containing 3% of  $\gamma$ -APS ( $\gamma$ -aminopropyltrimethoxysilane), and an excess of the  $\gamma$ -APS solution was readily squeezed off by using squeeze rolls to obtain a surface-treated steel plate having a silane coupling agent-treated layer containing Si in an amount of  $5 \text{ mg/m}^2$ . Next, the surface-treated steel plate was heated at  $225^\circ\text{C}$  which was lower than the melting point of tin by  $7^\circ\text{C}$  to heat-laminate a copolymerized polyester (m.p.,  $228^\circ\text{C}$ ) cast film comprising an undrawn copolymerized polyester (terephthalic acid/isophthalic acid (weight ratio of 88/12) and an ethylene glycol maintaining a thickness of  $20 \text{ }\mu\text{m}$  on both surfaces at a laminate roll temperature of  $150^\circ\text{C}$  and a passing speed of  $150 \text{ m/min.}$ , immediately followed by cooling with water to obtain a pre-coated steel plate. A wax-type lubricant was applied onto both surfaces of the pre-coated steel plate, and a disk of a diameter of 155 mm was punched by press to obtain a shallow drawn cup. Next, the shallow drawn cup was subjected to the stretch ironing to obtain a cup having a cup diameter of 66 mm, a cup height of 128 mm and an average plate thickness reduction ratio

of the can wall of 55%. The cup was subjected to the doming according to an ordinary method, heat-treated at 215°C, and was, then, left to cool, followed by the trimming of the open edge portion, printing on the curved surface, baking and drying, necking and flanging to obtain a can of a reduced thickness having a capacity of 350 g. Next, the can was filled with coke, and was double seamed with an end. After stored, the inner surface state of the can was examined.

Table 1 shows amounts of tin plated on the pre-coated steel plates, presence of reflow treatment, kinds of the surface treatment, thickness of treatment, kinds and thickness of organic coating materials, and Table 2 shows the evaluated results of the test of the cans.

[0032]

(Examples 2 to 5)

Pre-coated steel plates were prepared and cans were produced in the same manner as in Example 1 but varying the amount of tin plated on each surface as represented by the amounts shown in Table 1 and transforming part of the metal tin layer on the side of the steel plate into an iron-tin alloy layer by the reflow treatment, to evaluate them. The results were as shown in Table 2.

[0033]

(Example 6, Comparative Example 1)

Pre-coated steel plates were prepared and cans were produced in the same manner as in Example 1 but changing the amounts of tin plated on each surface as represented by the amounts shown in Table 1 to evaluate them. The results were as shown in Table 2.

[0034]

(Examples 7, 8 and 9, Comparative Examples 2 and 3)

Pre-coated steel plates were prepared and cans were produced in the same manner as in Example 1 but forming the silane coupling agent-treated layers containing Si in amounts as shown in Table 1 to evaluate them. The results were as shown in Table 2.

[0035]

(Example 10)

A pre-coated steel plate was prepared and a can was produced in the same manner as in Example 1 but treating the surface on the tin layer with a 3%  $\gamma$ -GPS ( $\gamma$ -glycidoxypropyltrimethoxysilane) water ethanol solution instead of using a  $\gamma$ -APS aqueous solution to evaluate them. The results were as shown in Table 2.

[0036]

(Example 11)

A pre-coated steel plate was prepared and a can was produced in the same manner as in Example 1 but treating the surface on the tin layer with a 3% BTSE (bis-1,2-(triethoxysilyl)ethane) water ethanol solution instead of using a  $\gamma$ -APS aqueous solution, followed by the treatment with a 3%  $\gamma$ -APS aqueous solution, and forming a film by the treatment containing Si in a total amount of 10 mg/m<sup>2</sup>, to evaluate them. The results were as shown in Table 2.

[0037]

(Example 12)

A pre-coated steel plate was prepared and a can was produced in the same manner as in Example 1 but treating the surface on the tin layer with a water ethanol solution of a mixture of 3% BTSPS (bistrimethoxysilylpropyltetra sulfide) and 3% APS instead of using a  $\gamma$ -APS aqueous solution, and forming a film by the treatment containing Si in an amount of 10 mg/m<sup>2</sup>, to evaluate them. The results were as shown in Table 2.

[0038]

(Comparative Example 4)

A pre-coated steel plate was prepared and a can was produced in the same manner as in Example 1 but treating the surface on the tin layer with a 3% tetraethoxysilane solution instead of using a  $\gamma$ -APS aqueous solution and forming a film by the treatment containing Si in an amount of 5 mg/m<sup>2</sup>, to evaluate them. The results were as shown in Table 2.

[0039]

(Comparative Example 5)

A pre-coated steel plate was prepared and a can was produced in the same manner as in Example 1 but treating the surface on the tin layer with a water ethanol solution of 3% BTSE (bis-1,2-(triethoxysilyl)ethane) instead of using a  $\gamma$ -APS aqueous solution, and forming a film by the treatment containing Si in an amount of 5 mg/m<sup>2</sup>, to evaluate them. The results were as shown in Table 2.

[0040]

(Comparative Example 6)

A pre-coated steel plate was prepared and a can was produced in the same manner as in Example 1 but subjecting the surface on the tin layer to the electrolytic phosphoric acid treatment instead of the treatment with the  $\gamma$ -APS aqueous solution and forming a film by the treatment containing P in an amount of 2.5 mg/m<sup>2</sup>, to evaluate them. The results were as shown in Table 2.

[0041]

(Comparative Example 7)

A resin-coated steel plate was prepared and a can was produced in the same manner as in Example 1 but subjecting the surface on the tin layer to the treatment with tin phosphate instead of the treatment with the  $\gamma$ -APS aqueous solution and forming a film by the treatment containing P in an amount of 2.5 mg/m<sup>2</sup> and Sn in an amount of 2.5 mg/m<sup>2</sup>, to evaluate them. The results were as shown in Table 2.

[0042]

(Examples 13 and 14, Comparative Examples 8 and 9)

Pre-coated steel plates were prepared and cans were produced in the same manner as in Example 1 but using an N- $\beta$  (aminoethyl)  $\gamma$ -aminopropyltrimethoxysilane as a silane coupling agent, forming a film by the treatment containing Si in an amount of 7 mg/m<sup>2</sup> and selecting the thickness of the copolymerized polyester film which is an organic coating material to be as shown in Table 1, to evaluate them. The

results were as shown in Table 2.

[0043]

(Example 15)

A pre-coated steel plate was prepared and a can was produced in the same manner as in Example 13 but selecting the kind and thickness of the polyester film which is the organic coating material as shown in Table 1, to evaluate them. The results were as shown in Table 2.

[0044]

(Example 16)

A pre-coated steel plate was prepared and a can was produced in the same manner as in Example 13 but using an undrawn homo PET (polyethylene terephthalate) film having a thickness of 25  $\mu\text{m}$  as an organic coating material, to evaluate them. The results were as shown in Table 2.

[0045]

(Example 17)

A pre-coated steel plate was prepared and a can was produced in the same manner as in Example 13 but selecting the kind and thickness of the biaxially drawn homo PET (polyethylene terephthalate) having a thickness of 25  $\mu\text{m}$  as an organic coating material as shown in Table 1, to evaluate them. The results were as shown in Table 2.

[0046]

(Comparative Example 10)

A pre-coated steel plate was prepared and a can was produced in the same manner as in Example 13 but using a polypropylene film having a thickness of 25  $\mu\text{m}$  as an organic coating material instead of using the copolymerized polyester film and laminating the films by using an urethane-type adhesive, to evaluate them. The results were as shown in Table 2.

[0047]

(Comparative Example 11)

A pre-coated steel plate was prepared and a can was produced in the same manner as in Example 13 but using a polyethylene film having a thickness of 25  $\mu\text{m}$  as an organic

coating material instead of using the copolymerized polyester film and laminating the films by using an urethane-type adhesive, to evaluate them. The results were as shown in Table 2.

[0048]

(Comparative Example 12)

A pre-coated steel plate was prepared and a can was produced in the same manner as in Example 13 but using an epoxyacrylic coating material as an organic coating material instead of the copolymerized polyester film, roll-coating the coating material in such an amount that the thickness after baking was 10  $\mu\text{m}$  and baking the coating material at 200°C for 10 minutes, to evaluate them. The results were as shown in Table 2.

[0049]

(Comparative Example 13)

A resin-coated steel plate was prepared and a can was produced in the same manner as in Example 13 but using an epoxyphenol-type coating material as an organic coating material instead of the copolymerized polyester film, roll-coating the coating material in such an amount that the thickness after baking was 10  $\mu\text{m}$  and baking the coating material at 200°C for 10 minutes, to evaluate them. The results were as shown in Table 2.

[0050]

(Comparative Example 14)

A resin-coated steel plate was prepared and a can was produced in the same manner as in Example 13 but using a vinylorganosol-type coating material as an organic coating material instead of the copolymerized polyester film, roll-coating the coating material in such an amount that the thickness after baking was 15  $\mu\text{m}$  and baking the coating material at 200°C for 10 minutes, to evaluate them. The results were as shown in Table 2.

Table 1

Sample	Tin-plating		Surface treatment		Organic coating material	
	Amount of tjn (g/m <sup>2</sup> )	ReFlow	Kind	Treating thickness (mg/m <sup>2</sup> )	Kind	Thickness (μm)
Ex. 1	0.5	no	γ-APS <sup>1)</sup>	Si, 5	PET/IA(12%) <sup>5)</sup>	20
Ex. 2	1.0	yes	γ-APS <sup>1)</sup>	Si, 5	PET/IA(12%) <sup>5)</sup>	20
Ex. 3	2.5	yes	γ-APS <sup>1)</sup>	Si, 5	PET/IA(12%) <sup>5)</sup>	20
Ex. 4	5.0	yes	γ-APS <sup>1)</sup>	Si, 5	PET/IA(12%) <sup>5)</sup>	20
Ex. 5	12.0	yes	γ-APS <sup>1)</sup>	Si, 5	PET/IA(12%) <sup>5)</sup>	20
Ex. 6	2.5	no	γ-APS <sup>1)</sup>	Si, 5	PET/IA(12%) <sup>5)</sup>	20
Comp.Ex.1	0.3	no	γ-APS <sup>1)</sup>	Si, 5	PET/IA(12%) <sup>5)</sup>	20
Ex. 7	2.5	yes	γ-APS <sup>1)</sup>	Si, 5	PET/IA(12%) <sup>5)</sup>	20
Ex. 8	2.5	yes	γ-APS <sup>1)</sup>	Si, 1	PET/IA(12%) <sup>5)</sup>	20
Ex. 9	2.5	yes	γ-APS <sup>1)</sup>	Si, 3	PET/IA(12%) <sup>5)</sup>	20
Comp.Ex.2	2.5	yes	γ-APS <sup>1)</sup>	Si, 15	PET/IA(12%) <sup>5)</sup>	20
Comp.Ex.3	2.5	yes	γ-APS <sup>1)</sup>	Si, 0.5	PET/IA(12%) <sup>5)</sup>	20
Ex. 10	2.5	yes	γ-APS <sup>1)</sup>	Si, 20	PET/IA(12%) <sup>5)</sup>	20
Ex. 11	2.5	yes	γ-GPS. <sup>2)</sup>	Si, 5	PET/IA(12%) <sup>5)</sup>	20
Ex. 12.	2.5	yes	BTSE <sup>3)</sup> → γ-APS 2-step treatment mixed solution of BTSPS, γ-APS tetraethoxysilane BTSE <sup>3)</sup> phosphoric acid tin phosphate	Si, 10	PET/IA(12%) <sup>5)</sup>	20
Comp.Ex.4	2.5	yes		Si, 10	PET/IA(12%) <sup>5)</sup>	20
Comp.Ex.5	2.5	yes		Si, 5	PET/IA(12%) <sup>5)</sup>	20
Comp.Ex.6	2.5	yes		Si, 5	PET/IA(12%) <sup>5)</sup>	20
Comp.Ex.7	2.5	yes		P, 2.5 P, 2.5 Sn, 2.5	PET/IA(12%) <sup>5)</sup>	20

1) γ-APS: silane coupling agent, γ-aminopropyltrimethoxysilane

2) γ-GPS: silane coupling agent, γ-glycidopropyltrimethoxysilane

3) BTSE: silane bis-1,2-(triethoxysilyl)ethane

4) BTSPS: silane bistrimethoxysilylpropyltetrasulfide

5) PET/IA(12%): polyethylene terephthalate/isophthalate

6) PET/IA(8%): polyethylene terephthalate/isophthalate (copolymerizing ratio, 12%)

7) Homo PET: homopolyethylene terephthalate (copolymerizing ratio, 8%)

8) N-β (aminoethyl) γ-APS: silane coupling agent N-β (aminoethyl) γ-aminopropyltrimethoxysilane



Table 1 (continued)

Sample	Tin-plating		Surface treatment		Organic coating material	
	Amount of tin (g/m <sup>2</sup> )	Reflow	Kind	Treating thickness (mg/m <sup>2</sup> )	Kind	Thickness (μm)
Ex. 13	2.5	yes	N-β (aminoethyl) γ-APS <sup>8)</sup>	Si, 7	PET/IA (12%) <sup>5)</sup>	10
Ex. 14	2.5	yes	N-β (aminoethyl) γ-APS <sup>8)</sup>	Si, 7	PET/IA (12%) <sup>5)</sup>	40
Comp. Ex. 8	2.5	yes	N-β (aminoethyl) γ-APS <sup>8)</sup>	Si, 7	PET/IA (12%) <sup>5)</sup>	7
Comp. Ex. 9	2.5	yes	N-β (aminoethyl) γ-APS <sup>8)</sup>	Si, 7	PET/IA (12%) <sup>5)</sup>	45
Ex. 15	2.5	yes	N-β (aminoethyl) γ-APS <sup>8)</sup>	Si, 7	PET/IA (8%) <sup>6)</sup>	25
Ex. 16	2.5	yes	N-β (aminoethyl) γ-APS <sup>8)</sup>	Si, 7	homo PET <sup>7)</sup>	25
Ex. 17	2.5	yes	N-β (aminoethyl) γ-APS <sup>8)</sup>	Si, 7	biaxially drawn homo PET	25
Comp. Ex. 10	2.5	yes	N-β (aminoethyl) γ-APS <sup>8)</sup>	Si, 7	polypropylene film	25
Comp. Ex. 11	2.5	yes	N-β (aminoethyl) γ-APS <sup>8)</sup>	Si, 7	polyethylene film	25
Comp. Ex. 12	2.5	yes	N-β (aminoethyl) γ-APS <sup>8)</sup>	Si, 7	epoxyacrylic paint	10
Comp. Ex. 13	2.5	yes	N-β (aminoethyl) γ-APS <sup>8)</sup>	Si, 7	epoxyphenol paint	10
Comp. Ex. 14	2.5	yes	N-β (aminoethyl) γ-APS <sup>8)</sup>	Si, 7	vinylorganosol	15

1) γ-APS: silane coupling agent, γ-aminopropyltrimethoxysilane

2) γ-GPS: silane coupling agent, γ-glycidoxypropyltrimethoxysilane

3) BTSE: silane bis-1,2-(triethoxysilyl)ethane

4) BTSPS: silane bistrimethoxysilylpropyltetrasulfide

5) PET/IA (12%): polyethylene terephthalate/isophthalate (copolymerizing ratio, 12%)

6) PET/IA (8%): polyethylene terephthalate/isophthalate (copolymerizing ratio, 8%)

7) Homo PET: homopolyethylene terephthalate

8) N-β (aminoethyl) γ-APS: silane coupling agent N-β (aminoethyl) γ-aminopropyltrimethoxysilane

Table 2

Experiment	Work adhesion property			Exposure of metal (mA)	Can testing	
	Can barrel	Necking portion	Flanging portion		Dissolved iron (ppm)	Inner surface of can
Ex. 1	○	○	○	0.00	0.00	normal
Ex. 2	○	○	○	0.00	0.00	normal
Ex. 3	○	○	○	0.00	0.00	normal
Ex. 4	○	○	○	0.00	0.00	normal
Ex. 5	○	○	○	0.00	0.00	normal
Ex. 6	○	○	○	0.00	0.00	normal
Comp. Ex. 1	○	○	△	0.10	0.70	double-seamed portion partly corroded
Ex. 7	○	○	○	0.00	0.00	normal
Ex. 8	○	○	○	0.00	0.00	normal
Ex. 9	○	○	○	0.00	0.00	normal
Comp. Ex. 2	○	△	×	3.56	5.65	necking portion, double-seamed portion partly corroded
Comp. Ex. 3	○	△	×	4.74	6.48	necking portion, double-seamed portion partly corroded
Ex. 10	○	○	○	0.00	0.00	normal
Ex. 11	○	○	○	0.00	0.00	normal
Ex. 12	○	○	○	0.00	0.00	normal
Comp. Ex. 4	△	△	×	5.43	6.82	necking portion, double-seamed portion corroded
Comp. Ex. 5	△	△	×	5.77	6.98	necking portion, double-seamed portion corroded
Comp. Ex. 6	△	×	×	6.29	8.17	necking portion, double-seamed portion corroded
Comp. Ex. 7	△	×	×	6.50	8.39	necking portion, double-seamed portion corroded

Table 2 (continued)

Experiment	Work adhesion property			Exposure of metal (mA)	Can testing	
	Can barrel	Necking portion	Flanging portion		Dissolved iron (ppm)	Inner surface of can
Ex.13	O	O	O	0.00	0.00	normal
Ex.14	O	O	O	0.00	0.00	normal
Comp.Ex.8	O	O	O	0.32	1.12	partly corroded under the film
Comp.Ex.9	O	Δ	Δ	2.16	1.67	necking portion, double-seamed portion corroded
Ex.15	O	O	O	0.00	0.00	normal
Ex.16	O	O	O	0.01	0.00	double-seamed portion partly and slightly discolored
Ex.17	O	O	O	0.02	0.01	double-seamed portion partly and slightly discolored
Comp.Ex.10	O	O	Δ	0.58	1.12	double-seamed portion corroded
Comp.Ex.11	O	O	Δ	0.63	2.18	double-seamed portion corroded
Comp.Ex.12	O	Δ	Δ	17.4	25.2	inner surface as a whole corroded
Comp.Ex.13	O	Δ	Δ	14.2	21.7	inner surface as a whole corroded
Comp.Ex.14	O	Δ	Δ	9.82	17.2	inner surface as a whole corroded

[0053]

Examples 1 to 6 and Comparative Example 1 have tested deep drawn cans having a reduced thickness made of pre-coated steel plates obtained by varying the amount of tin that is plated on the steel plates. It will be learned that excellent corrosion resistance and work adhesion property are exhibited when the cans are made of pre-coated steel plates plated with tin in an amount of 0.5 to 12.0 g/m<sup>2</sup>.

[0054]

Examples 1 to 6 are comparative experiments of when the reflow treatment is not effected after the tin plating and when the reflow treatment is effected to transform part of the tin layer on the side of the steel plate into a tin-iron alloy layer. It will be learned that excellent corrosion resistance and work adhesion property are exhibited by the stretch-ironed cans having a reduced thickness made of pre-coated steel plates when tin is plated in an amount of 0.5 to 12.0 g/m<sup>2</sup> on each surface.

[0055]

Examples 7, 8, 9 and Comparative Examples 2 and 3 have tested stretch-ironed cans having a reduced thickness made of pre-coated steel plates obtained by varying the thickness of the film treated with the silane coupling agent. It will be learned that the cans made of pre-coated steel plates containing Si in the film in an amount of 0.8 to 18 g/m<sup>2</sup> exhibit superior corrosion resistance and work adhesion property to those of the cans made of pre-coated steel plates having a film of a thickness without lying in the above range.

[0056]

Examples 10, 11, 12 and Comparative Examples 4, 5, 6 and 7 have tested stretch-ironed cans having a reduced thickness made of pre-coated steel plates obtained by using surface treating agents of different kinds. It will be learned that the cans made of pre-coated steel plates obtained by using an organosilane coupling agent containing a reaction group such as amino group or epoxy group and a hydrolyzing alkoxyl group exhibit superior corrosion resistance and work adhesion

property to those of the cans made of pre-coated steel plates obtained by using a silane treating agent without containing such groups, by using a phosphoric acid treating agent, or by using a tin phosphate treating agent.

[0057]

Examples 13, 14 and Comparative Examples 8 and 9 have tested the stretch-ironed cans having a reduced thickness made of pre-coated steel plates obtained by varying the thickness of the copolymerized polyester film. It will be learned that the cans made of a pre-coated steel plate coated with the polyester film of a thickness of 8 to 42  $\mu\text{m}$  exhibit superior corrosion resistance and work adhesion property to those of the cans made of the pre-coated steel plates coated with the polyester film having a thickness without lying in the above range.

[0058]

Examples 15, 16, 17 and Comparative Examples 10, 11, 12, 13 and 14 have tested the stretch-ironed cans having a reduced thickness made of pre-coated steel plates obtained by using organic coating materials of different kinds. It will be learned that the cans made of a pre-coated steel plate coated with the organic coating material of polyester exhibit superior corrosion resistance and work adhesion property to those of the cans made of the pre-coated steel plates coated with films or coating materials of other kinds. As the polyester, further, it will be learned that the most excellent properties are exhibited by the non-oriented polyethylene terephthalate type copolymerized film.

[0059]

#### [Effect of the Invention]

A press-formed can of the present invention is produced by using a pre-coated steel plate which is obtained by providing, on the surface of the steel plate on at least the side that becomes the inner surface of the can, a tin-plated layer containing tin in an amount of 0.5 to 12.0 g/m<sup>2</sup>, a silane coupling agent-treated layer containing Si in an amount of 0.8 to 18 mg/m<sup>2</sup>,

and a thermoplastic polyester resin layer having a thickness of 8 to 42  $\mu\text{m}$  in this order from the side of the steel plate. Therefore, there is produced a can featuring excellent work adhesion property of the film as well as excellent workability and corrosion resistance even when the thickness is reduced through a severe working such as draw-ironing, redrawing for reducing the thickness, or stretch-ironing even in those portions that are subjected to a severe working such as flanging and necking.

[Brief Description of the Drawings]

[Fig. 1] is a sectional view illustrating a pre-coated steel plate used for the present invention.

[Fig. 2] is a view illustrating another pre-coated steel plate used for the present invention.

[Designation of Document] Abstract

[Abstract]

[Problem] To provide a can obtained by press-forming a chrome-free steel plate coated with an organic resin featuring excellent film adhesion property, workability and corrosion resistance even when the thickness is reduced through severe working.

[Means for Solution]

A can having excellent corrosion resistance formed by press-forming a pre-coated steel plate which is obtained by providing, on the surface of the steel plate on at least the side that becomes the inner surface of the can, a tin-plated layer containing tin in an amount of 0.5 to 12.0 g/m<sup>2</sup>, a silane coupling agent-treated layer containing Si in an amount of 0.8 to 18 mg/m<sup>2</sup>, and a thermoplastic polyester resin layer having a thickness of 8 to 42  $\mu$ m in this order from the side of the steel plate.

[Selected Drawing] None